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8901 Wisconsin Avenue
Bethesda, MD 20889-5607

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ANALYSIS OF VOLATILE CONTAMINANTS IN U. S. NAVY FLEET SODA LIME

R. S. Lillo
R. Ruby
D. D. Gummin
W. R. Porter
J. M. Caldwell

Naval Medical Research
and Development Command
Bethesda, Maryland 20889-5606

Department of the Navy
Naval Medical Command
Washington, DC 20372-5210



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The experiments reported herein were conducted according to the principles set forth in the current edition of the "Guide for the Care and Use of Laboratory Animals," Institute of Laboratory Animal Resources, National Research Council.

This technical report has been reviewed by the NMRI scientific and public affairs staff and is approved for publication. It is releasable to the National Technical Information Service where it will be available to the general public, including foreign nations.

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13. ABSTRACT (Maximum 200 words) Contamination was suspected of U.S. Navy Fleet soda lime (High Performance Sodasorb®) when an ammonia-like odor was reported during its use in August 1992. This material contained indicator dye and was used for carbon dioxide absorption during diving. This incident had a major impact on the U.S Navy diving program when the Navy temporarily banned use of Sodasorb® and authorized Sofnolime® as an interim replacement. The Naval Medical Research Institute was immediately assigned to investigate. Testing involved sampling from the headspace (gas space) inside closed buckets and from an apparatus simulating conditions during operational diving. Volatile organic compounds were analyzed by gas chromatography and mass spectrometry; ammonia and amines were measured by infrared spectroscopy. Significant amounts of ammonia (up to 30 ppm), ethyl and diethyl amines (up to several ppm), and various aliphatic hydrocarbons (up to 60 ppm) were detected during testing of both Sodasorb® and Sofnolime®. Contaminants were slowly removed by gas flow and did not return. The source(s) of the ammonia and amines are unknown, although they may result from the breakdown of the indicator dye. Hydrocarbon contamination appeared to result from the materials of which the bucket is constructed. Based on these findings, the U.S. Navy is expected to phase in non-indicating soda lime that will be required to meet defined contaminant limits. This report presents: 1) in-depth description of procedures used during the investigation for contaminant analysis and 2) detailed results from all samples tested.					
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INTRODUCTION

Soda lime is widely used as a carbon dioxide (CO₂) absorbent in underwater breathing systems and hyperbaric facilities. For the past few years, the U.S. Navy has purchased most of its soda lime for diving from one manufacturer (W.R. Grace & Co., Lexington, MA). This soda lime was loosely packaged in high-density polyethylene, 5-gallon, round buckets with a net weight of 37 lb. The absorbent (High Performance Sodasorb®) contained the indicator dye, ethyl violet, to allow users to monitor by color change the decline in CO₂ absorbent capacity of the soda lime. Anecdotal information suggests that the amount of indicator dye in Fleet Sodasorb® has increased over time, which is confirmed by a recent report from the manufacturer (1). Unfortunately, the latest Department of Defense specification on soda lime (2), written in 1953, is not applicable to present requirements and practices, including packaging and type of indicator dye. For these reasons, soda lime for diving use has been procured for a number of years by the U.S. Navy without a detailed military specification and, thus, without defined levels for indicator dye.

Contamination of U.S. Navy Fleet soda lime was suspected when an ammonia-like odor was reported during its use in August 1992 (3). At that time, there was also concern that there might be amines present in the soda lime and questions arose regarding the relationship of contaminants to indicator dye. Preliminary screening of suspected lots of Sodasorb® by the Naval Medical Research Institute (NMRI) also revealed the presence of significant volatile hydrocarbons. Despite initial requests to the manufacturer for assistance and guidance, the issue remained unresolved. Therefore, in September 1992 the Chief of Naval Operations commissioned the Naval Medical Research and Development Command (NMRDC) to

investigate the issue. In October 1992 the responsibility for conducting the investigation was assigned to NMRI by NMRDC. The suspected contamination had a major impact on the U.S. Navy diving program when the Naval Sea Systems Command (NAVSEA) temporarily banned use of Sodasorb®. Sofnolime®, another brand of soda lime containing ethyl violet (Molecular Products Ltd., Essex, U.K.), was authorized as an interim replacement (4).

Our investigation was performed from Oct 1992 to May 1994 and had three main objectives:

- 1) Identify all potentially dangerous contaminants in Fleet soda lime.
- 2) Determine whether the indicator dye or the buckets are sources of contamination.
- 3) Recommend solutions to insure chemically safe soda lime for Fleet diving.

Preliminary findings, along with interim recommendations, have been reported previously to NAVSEA (5-7). A summary of our results and discussion of their significance for U.S. Navy diving are under review (8). In response, the U.S. Navy is expected soon to phase in, for all diving, non-indicating soda lime that will be required to meet specific contaminant limits (9). In contrast, this report provides expanded information on the analytical procedures used during the investigation and detailed results from all samples tested. Some of the information reported elsewhere (8) has been included here to produce a stand-alone document.

METHODS

Soda lime samples

Soda lime test samples were taken from 5-gallon buckets made of high-density polyethylene that were obtained from U.S. Navy supply stock or from the manufacturer:

1) High performance Sodasorb®

- a) 25 lots of 4-8 mesh granules
- b) with and without indicator dye
- c) packaged in 42 round buckets.

2) Sofnolime®

- a) 25 lots of 4-8 mesh granules (L grade) in 34 round or square buckets
- b) 3 lots of 8-12 mesh granules (D grade) in 5 square buckets
- c) all but 2 buckets containing indicator dye.

All Sodasorb® buckets were acquired full and unopened prior to testing; a few of the Sofnolime® buckets had been previously opened and partially used for Fleet diving. Buckets and lids were marked as to the month of their manufacture.

Sodasorb®

Sodasorb® samples were produced between April 1991 and July 1993, which included a number of lots without indicator dye made specifically for the Navy. A "lot" is all the soda lime made during one shift (\leq one day) of the manufacturing plant. Practically, there may have been more than one lot produced during a single day. Some of the non-indicator lots were packaged in canister bags that were then put inside the high-density polyethylene buckets (10 bags per bucket). Canister bags are laminated and comprised of paper, aluminum, and plastic. Each bag contains approximately 1350 g of soda lime. This bags-in-bucket packing was proposed by the manufacturer of Sodasorb® as an alternative packaging method. All buckets and lids were made by one supplier (Bennett Industries, Inc., San Fernando, CA).

In addition to full buckets, a number of unused, empty buckets identical to those used for packaging soda lime were obtained and tested after lids had been in place for at least 1 week. **Appendix A** lists each Sodasorb[®] bucket that was sampled and discussed in this report by the following information: NMRI in-house bucket code, manufacturer lot number, date of soda lime manufacture (derived from lot number), and month of manufacture of bucket and lid (marked on the outside bottom of the bucket and inside lid surface). Lid dating required the removal of the lid from the bucket for a brief time (e.g., less than 30 s).

Sofnolime[®]

Sofnolime[®] samples were produced from September 1991 to December 1993. These included 2 buckets without indicating dye that were also made especially for the Navy. Sofnolime[®] was obtained either in round buckets (Fein Plastic Can Corp., currently a subsidiary of Bennett Industries) similar to those used for Sodasorb[®], or in square containers (Blowmogan, Milton Keynes, U.K.), which had a removable cap on the pour spout rather than a lid. The round buckets were filled in the U.S. with absorbent, whereas the square buckets were packaged in the U.K. **Appendix B** lists each bucket of Sofnolime[®] in the same fashion as for Sodasorb[®], except that lids were not removed. Therefore, lid dates are omitted.

Soda lime contaminant testing

Two types of contaminant tests were performed during this investigation: headspace testing and contaminant washout.

Headspace testing

Gas was initially sampled from the headspaces (gas spaces) inside closed buckets of

soda lime. These samples were subsequently analyzed to identify and quantify volatile organic compounds using gas chromatography (GC). Samples were taken using either 1) 500-ml stainless steel cylinders that had been previously heated and evacuated to at least 30 millitorr or 2) 150-ml passivated stainless steel syringes (Scientific Instrumentation Specialists, Moscow, ID). A specially designed stainless steel adaptor with an 18-gauge needle was inserted through the lid and penetrated approximately 3.5 cm into the bucket space. A rubber gasket at the base on the needle formed a tight seal preventing outside air from being drawn into the bucket during sampling. Preliminary GC testing showed that there was no observable effect of the adaptor on either ppm level hydrocarbon mixtures or hydrocarbon-free gas that were flowed through it. Headspace samples were drawn following attachment to the adaptor of either an evacuated cylinder or a syringe that had been purged 3 times with hydrocarbon-free gas. For cylinder sampling, the cylinder valve was opened slowly, 1 min then allowed for equilibration, and the valve closed before removal from the bucket. For syringe sampling, the syringe was filled with approximately 50 ml of bucket gas, expelled to the atmosphere, and then filled completely (150 ml) before removal.

Upon removal of the bucket adaptor, air was occasionally heard entering the bucket, suggesting that negative pressure had developed during sampling and that cylinders may have been equilibrated at less than atmospheric pressure. In other cases, leaks may have allowed laboratory air to enter the bucket during both cylinder and syringe sampling. For these reasons, levels of organic compounds measured in the headspace samples may be somewhat lower than actual concentrations inside the bucket prior to sampling. Following sampling, the needle hole in the bucket lid was sealed externally using a GC rubber septum and high-

strength adhesive-backed tape.

Headspace samples were not analyzed for ammonia and amines, because our method of analysis, using Fourier Transform Infrared (FTIR) spectroscopy, required a constant flow to produce reliable data as discussed below. No reliable method was developed to allow GC analysis of ammonia and amines.

Contaminant washout

A method was subsequently developed to measure contaminant washout as humidified 5% CO₂ in hydrocarbon-free air flowed through a bed of soda lime using the test apparatus shown in **Figure 1**. This apparatus, with a total internal chamber volume of 11.2 l, was designed to simulate conditions that might occur during actual use of the absorbent in order to help estimate exposures during diving. The gas was directed through the bed at 5 l/min, out through the gas cell where FTIR analysis occurred, and then vented into the atmosphere. Ammonia, amines, and total hydrocarbons were measured using FTIR; gas was also sampled for subsequent detailed analysis of volatile organic compounds by GC.

The test apparatus was loaded by first opening the bucket spout and pouring soda lime into a tared metal pan that was then covered with a metal lid and weighed to 2500 ± 10 g on a triple-beam or electronic balance. The bucket spout was immediately closed following soda lime transfer. Following weighing, the test apparatus was filled with the soda lime and sealed. These steps were completed quickly (generally less than 10 min) to minimize offgassing of the soda lime.

This was an open system where contaminants were flushed from the soda lime rather than allowed to recirculate as they might in a closed-circuit breathing device. As gas

continuously flowed through the FTIR, frequency of measurements was only limited by the time required for the FTIR quantitation program to complete 1 cycle, which was slightly less than 3 min. Soda lime samples were required to be analyzed in the test apparatus for at least 20 min; usually this time was considerably longer (e.g., over 1 h), until ammonia and amine levels dropped to below 1 ppm. Prior to gas sampling for GC analysis, an open-ended adaptor was attached to the normally closed sample point (noted in **Figure 1**). This allowed approximately 100 ml/min of gas leaving the soda lime bed to flush the sample line for 40 s. The cylinder or pre-flushed syringe was then attached and sampling done the same as for headspaces, except for one difference: the syringe was first purged with a full 150 ml of sample gas before obtaining the actual sample vs. only a 50-ml purge for headspace samples to minimize the amount of gas removed from the closed bucket.

During each experiment, flow, dew point, and CO₂ level were determined for both input and output gas, and ambient laboratory and soda lime bed temperatures measured. Dew point was measured using a dew point hygrometer (model Hygro-M1, General Eastern Instruments, Woburn, MA). Carbon dioxide was measured in the output gas with an infrared CO₂ analyzer (model LI-6252 with model LI-670 flow control unit, LI-COR, Inc., Lincoln, NE), calibrated with a primary standard of 500 ppm CO₂ in air, to insure that the absorbent had scrubbed all CO₂ from the gas. Ambient laboratory and soda lime bed temperatures were measured using a Tele-thermometer (model 2100; Yellow Springs Instrument Co., Yellow Springs, OH). Flows were monitored with rotameters found accurate to within 10% of reading by measuring the volume of water the gas flow displaced from a graduated cylinder over a known time.

Gas chromatography

Gas samples were screened for a broad range of volatile organic compounds using Shimadzu GC-9A temperature-programmable gas chromatographs (Shimadzu Corp., Columbia, MD) with both flame ionization detection (FID) and mass spectrometry (MS). For GC/FID, gas samples (0.5 ml) were introduced using gas sample valves. For GC/MS (model 5970 Mass Selective Detector, Hewlett-Packard Co., Rockville, MD), 100 ml of gas was preconcentrated at 10 °C on a solid multibed carbon adsorbent (carbotrap 300; Supelco, Inc., Bellefonte, PA). Subsequent thermal desorption at 340 °C for 5 min (Nutech 8533 Universal Sample Concentrator, Nutech Corp., Durham, NC) introduced the sample into the GC. Mass spectrometer scanning was from 20 to 200 amu.

The following columns were used with the indicated detectors and temperature profiles:

1) Vocol wide-bore capillary column, 30 m x 0.53 mm, 3.0 µm film. FID: 50 °C for 3 min, raised at 8 °C/min to 150 °C for 4.5 min. GC/MS: -20 °C for 3.1 min, raised at 20 °C/min to 150 °C for 11.4 min

2) Supelcowax 10 wide-bore capillary column, 60 m x 0.53 mm, 1.0 µm film. FID: 50 °C for 3 min, raised at 8 °C/min to 150 °C for 5 min.

3) 1/8 inch x 10 ft stainless steel packed column with 3% SP-1500 on 80/120 carbopack packing. FID: 40 °C for 1 min, raised at 20 °C/min to 200 °C for 4 min.

All columns were obtained from Supelco, Inc.

Prior to analysis, all samples in stainless steel cylinders, which were near atmosphere pressure, were vented to atmosphere and then pressurized with 15 psig of hydrocarbon-free air

using a low-delivery pressure, high-purity regulator. Samples could then be delivered to the instruments via positive pressure from the cylinder. Quantitation was adjusted for this dilution effect by applying a correction factor based on the pressures or by performing identical venting/pressurizing procedures with the calibration mixtures. Preliminary testing with calibration mixtures demonstrated that such procedures introduced an additional error of no more than several percent relative of expected value.

During the initial part of this investigation, the same gas sample was simultaneously analyzed by GC/FID and GC/MS on the same GC using identical columns (Vocol) in order to determine whether all organic species, particularly the more volatile ones, were effectively trapped and released by the carbotrap 300 adsorbent. Both analytical methods appeared to produce similar results in terms of numbers of peaks detected, the general appearance of the chromatograms, and quantitation, except as described below. Exact retention times were different, however, as would be expected since injection methods were different (i.e., gas valve injection vs. thermal desorption). Once this agreement was confirmed, GC/MS was used exclusively because of its increased sensitivity due to preconcentration and the ability to generate mass spectra to facilitate identification.

Identification of organic species was based on comparison of retention times of sample peaks and of species in commercially acquired, primary gas standards. All identifications were confirmed by comparison of mass spectra. Unknown compounds that did not match retention times of the standards were identified after careful review of library search results using Hewlett-Packard G1034B or G1034C software for the MS ChemStation (DOS series) with the NIST/EPA/MSDC 54K Mass Spectral Database and in view of the limitations inherent in

such searches. Unfortunately, for many of the components of the complex mixtures found in samples, it was not practical to confirm the search results by injection of the pure chemicals into the GC/MS.

Quantitation of volatile organic compounds by GC was based on GC/MS analysis with a conservative reporting limit of 0.1 ppm. When present, hexane, octane, and decane were individually quantified using a gravimetric standard, certified to $\pm 2\%$ relative, containing 2 ppm each of these compounds in hydrocarbon-free air (Scott Specialty Gases, Plumsteadville, PA). The remaining straight-chained and branched hydrocarbons that were found were expressed both in terms of octane and decane equivalents by quantifying the sum of their peak areas relative to the areas of octane and decane in the calibration standard. Concentrations expressed in these two ways were generally within 10-20% of each other. Other contaminants that were detected, but estimated to be below the reporting limit, were not quantified.

Thermal desorption from carbotrap 300, as used in this investigation during GC/MS, was not effective in removing all the heavy molecular hydrocarbons (decane and above). For this reason, GC/MS quantitation of the few samples with hydrocarbons levels much higher than the calibration standard (2 ppm) may be low by up to an estimated 30% relative. This estimate is based on 1) comparative GC/FID data, 2) comparative GC/MS data from direct loop injection, and 3) repeat thermal desorption and subsequent GC/MS analysis of a single sample to estimate the amount of residual hydrocarbons not desorbed during the first analysis. For quantitation of samples with hydrocarbon concentrations of several ppm or less, the error in quantitation is estimated to be less than $\pm 20\%$ relative.

Precision for GC/MS was checked at the start of each day by performing two consecutive analyses of 100 ml of a primary standard of 2 ppm each of Freon 113, methyl chloroform, benzene, toluene, and xylenes. Percent coefficients of variation (%CV) for peak areas, where $\%CV = 100 * (\text{difference between the 2 injections}) / (\text{mean of the 2 injections})$, were generally better than 10%. Gas Chromatography/MS responses were shown to be linear to within 10% over a range from 1 - 2 ppm each of hexane, octane, and decane. Detectability limits for GC/MS are estimated to be less than 0.05 ppm for hexane, octane, and decane.

FTIR analysis

FTIR analysis (model 1600 FT-IR, Perkin Elmer Corp., Norwalk, CT) with a 20-meter gas cell was used to measure ammonia, ethyl amine, diethyl amine, octane (as a measure of total hydrocarbons) and water, which was included to account for its interference in samples. The FTIR was calibrated each day using QUANT software supplied with the instrument, which applies curve-fitting to data from a defined spectra window rather than from one discrete frequency. Calibration used the following gravimetric standards obtained commercially from several sources and individually prepared in hydrocarbon-free air: 5 to 30 ppm ammonia, 5 and 10 ppm ethyl amine, 5 to 10 ppm diethyl amine, and 10 ppm octane, all certified to 2% relative, and 100% humidified air (hydrocarbon-free) for water. The actual ammonia standards used for calibration depended on the expected ammonia concentrations of the samples. When indicating dye was present in the soda lime, the higher ammonia standards (e.g., 10 ppm and 20 or 30 ppm) were used to quantitate the relatively high ammonia found. When indicating dye was absent, the lower ammonia standards (e.g., 5 and 10 ppm) were

used as little ammonia was usually found. In this case, only a single value for total hydrocarbons was derived from the infrared spectrum that was used to gauge washout time rather than to characterize the hydrocarbon profile that was done by GC. Amines were not measured during the early phase of this study, due to problems in method development.

All scans were ratioed to a background spectrum that was obtained at the start of each day after the gas cell had been evacuated to < 1 millitorr. Spectra were recorded with 2 cm^{-1} resolution from 4000 to 700 cm^{-1} . Calibration windows for all components were set from 1200 to 800 cm^{-1} , except for octane, which was from 3050 to 2750 cm^{-1} . Each quantitation cycle was completed in less than 3 min and produced 1 measurement for each of the 5 components.

Performance testing and experience acquired through use of the FTIR with the 20-meter gas cell demonstrated the unreliability of measurements under no-flow conditions. Declines in analyte levels when flow was stopped was a particular problem with reactive species such as ammonia and the amines that presumably adsorbed to the interior surfaces of the gas cell. For these reasons, all calibration and analyses of the FTIR were done with gas flowing through the cell except for special testing where noted.

FTIR measurements for all analytes, except water, were shown to be linear to within 0.5 ppm absolute or better over the concentration ranges of the standards by using a precision gas divider (STEC model SGD-710, Horiba Instruments, Inc., Ann Arbor, MI). The STEC device allowed blending of the calibration gas with a diluent gas in 10 equal steps from 0% to 100% of the original concentration and has been previously shown to be linear to within the manufacturer's specification of $\pm 0.5\%$ of full scale, using 10 to 100 ppm gas standards of

several hydrocarbon species (10). Here, dry air, 100% humidified air, and the 30-ppm ammonia standard were all used as diluent gases with the gas flowing from the divider directly into the gas cell. The wet air and ammonia dilutions demonstrated that high water and ammonia, present during soda lime analysis, did not interfere with quantitation of the other analytes.

Recovery of octane, ammonia, and the two amines following passage through the apparatus was determined by flowing the calibration standards (dry) at 5 l/min directly into the inlet side of the empty test chamber and measuring their concentrations in the 20-meter gas cell after 10 min. Measured concentrations in the cell were within 2% relative of the concentrations of the standards. Baseline composition of the test apparatus was also determined by flowing hydrocarbon-free air through the water bubbler and empty test chamber; during this octane, ammonia, and the two amines were monitored for at least 15 min. None of the 4 analytes were detected (< 0.1 ppm) with FTIR and no volatile organics were detected (< 0.05 ppm) with GC/MS.

Preliminary testing demonstrated that FTIR measurements reached 99% of full response after 3 quantitation cycles or less than 9 min following switching the gas cell initially filled with ammonia-free gas to a 5 to 30 ppm ammonia standard delivered at 5 l/min. Similar response times were observed for washout to reach levels < 0.1 ppm when the reverse switch from ammonia standard to ammonia-free gas was done. The FTIR output was also monitored as a trace chloroform mixture (< 1 ppm octane equivalent) that was introduced into the empty soda lime vessel of the test apparatus was flushed out through the gas cell with 5 l/min of hydrocarbon-free gas. Again, after less than 9 min, octane equivalent levels

fell below 0.1 ppm (FTIR). Complete removal of chloroform by this time was confirmed by analyzing gas samples with GC/MS.

The reliability of FTIR procedures for analysis of gas mixtures such as those from soda lime was also investigated by preparing "synthetic" gas mixtures inside the gas cell using the primary gas standards. Approximately equal partial pressures of 10 ppm octane, 10 ppm ammonia, 5 ppm of both ethyl and diethyl amines, and dry or 100% humidified air were added to the previously evacuated gas cell using a high-precision pressure gauge (models #122AA-00010AB and #122AA-01000AB, MKS Instruments, Inc., Andover, MA) to a final pressure of approximately 1.3 atm. All gas additions were completed within 5 min, and FTIR analysis was performed during the following 40 min under no-flow conditions. Measured values were compared to calculated values based on the partial pressure of each component added to the mixture. Measured values immediately after mixing were found to equal on average 99%/100% (using dry air/using wet air) of the calculated octane level, 91%/87% of ammonia, 111%/100% of diethyl amine, and 135%/113% of ethyl amine. These are based on 3 tests each with dry and wet air. Concentrations, especially those of ammonia, then dropped with time as analytes presumably interacted with the interior of the gas cell. By 40 min, measured octane (dry air/wet air) was 97%/99% of calculated value, ammonia 72%/71%, diethyl amine 93/91%, and ethyl amine 121%/92%.

Based on the preceding tests and experience using these procedures, FTIR lower reporting limits are conservatively defined as 0.5 ppm for octane, ammonia, and diethyl amine, and 1 ppm for ethyl amine. Analytical accuracy is conservatively estimated as ± 0.5 ppm absolute for octane, ammonia, and diethyl amine, and ± 1 ppm for ethyl amine for the

concentration ranges measured.

Dye testing

Soda lime samples were analyzed for ethyl violet dye, using methods we previously described (9), to help clarify the potential role that the dye played in the contamination problem. All dye measurements were performed in March-May 1994 following completion of testing for gaseous contaminants.

RESULTS

Test apparatus conditions

During washout experiments with the test apparatus in which 5 l/min of 5% CO₂ in air flowed through a 2500-gram bed of soda lime, the following conditions were recorded.

1) Laboratory temperature: 19-27 °C

2) Soda lime bed temperature:

Starting: laboratory temperature \pm 0.5 °C

Post 60-min flow: 31-36 °C

3) CO₂ in output flow from soda lime bed:

< 0.01% for the duration of the test

4) Dew point

Input gas to soda lime bed: 0.5 °C below laboratory temperature

Output gas from soda lime bed: 19-21 °C

Volatile Organic Compounds

Sodasorb[®]

At least 3 different hydrocarbon profiles were found in headspace samples from Sodasorb[®] (**Table 1** and **Figure 2**). These profiles are defined based on the predominant species present:

1) Approximately 1 - 2 ppm of a range of hydrocarbons including hexane, octane, and decane, and < 1 ppm of a highly volatile species identified as a butene isomer by its mass spectra. The majority of Sodasorb[®] samples had this profile.

2) Approximately 30 - 60 ppm of a complex mixture of aliphatic hydrocarbons with 7 - 10 carbon atoms/molecule. This profile characterizes one lot of indicating Sodasorb[®] made in 1991.

3) Approximately 5-10 ppm of a complex mixture of aliphatic hydrocarbons with 9 - 13 carbon atoms/molecule and again < 1 ppm of the butene isomer. This profile characterized a) another lot of indicating Sodasorb[®] made in 1992, b) all the non-indicating Sodasorb[®] made in 1992 and 1993 that was tested, and c) "virgin" buckets made in 1 month in 1992, but never exposed to soda lime (NMRI's codes: GPE1 and GPE2). Buckets made the same month as these latter ones had been used for packaging some of the non-indicating Sodasorb[®].

Headspace measurements repeated up to 6 months following the first samples generally agreed to within the level of analytical precision although the large difference in replicates for bucket N6 suggests an error in sampling. Hydrocarbon levels measured in gas flowing out of a bed of Sodasorb[®] were generally lower than those measured from the headspace of the same bucket (**Table 2**). Hydrocarbons more volatile than decane appear

easily removed by gas flow as they were absent or much reduced in washout samples.

The similarity in the hydrocarbon profiles of "virgin" buckets and Sodasorb® packaged in buckets made the same and different months suggests the bucket was the contaminant source. Unfortunately, older "virgin" buckets were not available to allow comparison with earlier lots of Fleet soda lime. However, our testing revealed another case where hydrocarbon profiles of the same lot of soda lime varied when packaged in buckets manufactured in different months (compare buckets BB4 and BB4D with buckets BB4C and BB4F in Table 2). The role of the bucket lids was not evident from the data, but would be confounded by the buckets.

In addition to the main contaminants distinguishing the profiles, most samples also contained low levels (< 0.1 ppm) of a number of other organic contaminants that were similar among all buckets. These included several alcohols and tetrahydrofuran. The majority of hydrocarbons may originate either from residual monomers from the bucket polymer or as processing aids used during the blow molding manufacturing process. These would include hexane, octane, decane, and the complex hydrocarbons mixtures. The alcohols (methanol, ethanol, and isopropyl) may be residual materials present in the Sodasorb® itself. Tetrahydrofuran and some of the other compounds may have been components of the ink used to mark the outside of the buckets.

Sodasorb® alternative packaging

Early test data by NMRI implicating the bucket as a problem prompted the manufacturer of Sodasorb® to propose an alternative packaging method using the canister bags described earlier. This was to be an interim packaging method (thus, all such buckets are

coded "IP#") until a long-term solution could be found. The 3-layer bags were to provide a barrier preventing or reducing hydrocarbon pickup by the soda lime from the bucket. Testing revealed that Sodasorb®, packaged this way and initially found to be hydrocarbon-free, slowly picked up hydrocarbon contaminants (profile 3) when the bags were placed into buckets. This resulted in absorbent gas concentrations of over 50% of bucket headspace concentrations after less than 3 months. This method was obviously not very effective in insuring hydrocarbon-free material over normal storage periods (e.g., several years).

Sofnolime®

At least 3 different hydrocarbon profiles were also found in headspace samples from Sofnolime® (Table 3):

1) Approximately 1 - 2 ppm of a range of hydrocarbons including hexane, octane, and decane, and < 2 ppm butene isomer. All Sofnolime® from round buckets had this profile, which appeared identical to Profile 1 of Sodasorb®.

2) Approximately 1 - 3 ppm of a mixture of aliphatic hydrocarbons with up to 10 carbon atoms/molecule. No hexane, octane, or decane were detected. Mass spectra search results suggested that many of the contaminants were unsaturated or cyclic in nature. Sofnolime® from all but one of the square containers had this profile.

3) Approximately 5 ppm of a complex mixture of aliphatic hydrocarbons with 7 - 9 carbons/molecule and < 0.5 ppm methyl chloroform. This profile characterizes one lot of Sofnolime® made in 1992 and packaged in square containers.

As with Sodasorb®, most samples also contained low levels (< 0.1 ppm) of a number of other organic contaminants, and hydrocarbon levels measured during washout were usually

lower than headspace concentrations.

Washout curves

Sodasorb[®]

Peak ammonia levels during washout from a test bed of indicating Sodasorb[®] ranged from 5 - 29 ppm, with an overall average of 17 ppm for samples taken from 23 buckets representing 16 different lots (Table 4). It generally took over 1 h of gas flow for ammonia to wash out to below 1 ppm. In a few instances, ammonia levels remained above 25 ppm for over 15 min. All detectible hydrocarbons (i.e., octane) were usually removed after 20 to 50 min of gas flow. Peak diethyl amine levels varied up to 4 ppm, with the washout curve generally tracking that of ammonia. Maximum ethyl amine levels ranged up to 2 ppm, although these values should be viewed in the context of an estimated analytical error of ± 1 ppm, which is twice that of ammonia and diethyl amine.

Washout curves consistently show longer washout times for the polar ammonia and amines than for the hydrocarbons, which may be due the increased adsorbance of soda lime for these compounds. Retesting up to 3 days after washout produced no evidence of contaminant regeneration. Two samples from the same bucket run back-to-back on the same day produced peak ammonia values that were always within 5% of each other (Table 5) and washout curves that generally agreed within the level of analytical precision. Samples from the same bucket over a period of less than a year generally agreed to within several ppm ammonia and 1 ppm octane (Table 4). The few large declines in subsequent ammonia measurements can be attributed to loss of volatiles from buckets that were not effectively

sealed, as substantial drops in octane measurements also were noted. However, considerable variation in contaminant levels was often observed among buckets containing soda lime from the same lot. FTIR estimates of total hydrocarbons in octane equivalents agree well with the GC data despite the analytical error and differences in technique (compare GC data in **Table 2** with FTIR octane data in **Tables 4 and 6**).

No more than 1 ppm ammonia was detected in the gas during testing of non-indicator absorbent from 12 buckets representing 8 lots (**Table 6**). Peak diethyl and ethyl amine levels during washout from non-indicating Sodasorb® were both less than the respective reporting limits (0.5 and 1.0 ppm).

Sofnolime®

Peak ammonia levels during washout from indicating Sofnolime® ranged up to 3 ppm with an overall average of 1 ppm for samples taken from 25 buckets (**Table 7**). These ammonia levels were much lower than those found in indicating Sodasorb®. Washout curves for samples with several ppm ammonia were similar to those for Sodasorb®, although such washouts are poorly defined when ammonia levels are this low. Peak diethyl and ethyl amine levels in indicating Sofnolime® varied up to 3 and 1 ppm, respectively; these concentrations are similar to those from indicating Sodasorb®. No ammonia or amines above the reporting limits were measured in samples from the 2 buckets of non-indicator material.

Ethyl violet dye

Ethyl violet measurements for indicating soda lime ranged from 0.011 to 0.030% with no significant difference ($p < 0.01$) between Sodasorb® and Sofnolime® (**Tables 8-9**).

Unfortunately, dye analysis was done at the end of this investigation and only a few of the buckets containing indicating Sodorb® were still left for testing. All buckets of soda lime supplied as non-indicator material were found to be free of dye as defined in reference (9).

DISCUSSION

Significant amounts of ammonia, ethyl and diethyl amines, and various aliphatic hydrocarbons were measured in gas samples from Fleet soda lime. The source(s) of the ammonia and amines are unknown, although one hypothesis is that they result from the breakdown of the indicator dye during manufacture, processing, or storage. This hypothesis is supported by the relatively low levels of ammonia and amines associated with all non-indicator soda lime as well by tests by one manufacturer of soda lime showing a strong correlation between dye decomposition and ammonia generation (1). Modeling results of these data suggest that peak diethyl amine concentrations and the amount of indicating dye in soda lime can be significant predictors of peak ammonia concentrations (8). However, it is interesting that amine and ethyl violet levels were similar in Sodorb® and Sofnolime®, although ammonia levels were greatly different. Thus, contaminant relationships appear different for the 2 brands of soda lime. Such findings do not establish cause and effect, and it must be emphasized that a causative link between the indicator dye and such contamination has not yet been demonstrated.

All of the test samples of soda lime gave off varying amounts of aliphatic hydrocarbons which, in the case of recently manufactured Sodorb®, appear to arise from the high-density polyethylene buckets. A direct link between buckets and hydrocarbon

contamination of past lots could not be made due to unavailability of older buckets never exposed to soda lime. However, the difference between Sofnolime[®] packaged in round vs. square buckets implicates the container as the source of the hydrocarbon contamination. Such contaminants are believed to come from the material used for construction of the bucket as was underscored by the experience with the canister bag packaging for Sodasorb[®].

Samples of soda lime and buckets manufactured earlier than mid-1991 were unavailable, making the history of the contamination problem unclear. It is unknown whether the ammonia and/or amine problem with soda lime was the result of a change in the manufacturing process or past contamination had simply gone undetected. The variation in ammonia levels within and among soda lime lots may reflect, at least in part, differences in breakdown of indicator dye. Hydrocarbon contamination of soda lime was unexpectedly discovered during initial testing in response to the ammonia-like odor. Unfortunately, we have no information on what has occurred in the plant(s) that manufacture the high density polyethylene buckets that are used for soda lime.

REFERENCES

1. WR Grace & Co. Response to notification of investigation. May 13, 1993. FDA project number DD30054Z.
2. MIL-S-17063A (U.S.). Soda lime; for removal of carbon dioxide and chlorine from air and other gases. 5 June 1953.
3. Telephone conversation between J. Clarke of U.S. Navy Experimental Diving Unit, Panama City, FL and Naval Sea Systems Command, Office of U.S. Supervisor of Diving and Salvage, Arlington, VA.
4. U.S. Naval Sea Systems Command. Message 300003ZSEP92. Subj: HP Sodorb warning follow-up (Diving advisory 92-35). 30 Sept 1992.
5. Naval Medical Research Institute. Subj: Interim recommendations regarding Fleet Sodorb use. Letter 3150, Serial #04/30502 of 21 May 93.
6. Naval Medical Research Institute. Subj: Update on the Naval Medical Research Institute investigation of Fleet Sodorb. Letter 3900, Serial #05/30937 of 7 Oct 93.

7. Naval Medical Research Institute. Subj: Interim contaminant limits for procurement of Fleet soda lime. Letter 3900, Serial #54/33028 of 2 June 94.

8. Lillo, R.S., Ruby, A., Gummin, D.D., Porter, W.R., and Caldwell, J.M., "Chemical safety of U.S. Navy Fleet soda lime." Undersea and Hyperbaric Medicine (in review).

9. Lillo, R.S., Ruby, A., Gummin, D.D., Porter, W.R., Caldwell, J.M., Interim contaminant limits and testing procedures for U.S. Navy Fleet soda lime. NMRI Technical Report No. 95-02, Naval Medical Research Institute, Bethesda, MD, 1995.

10. Lillo, R.S., Caldwell, J.M. Preliminary evaluation of a halogen leak detector for screening divers' breathing air. NMRI Technical Report No. 89-108, Naval Medical Research Institute, Bethesda, MD, 1989.

Table 1. Hydrocarbon contaminants in bucket headspaces measured with GC. Sodasorb® with and without indicator dye.

NMRI Bucket Code	Hydrocarbon Profile	Test Date (month/year)	Butene (ppm)	Hexane (ppm)	Octane (ppm)	Decane (ppm)	Other HC's in Octane Equiv. (ppm)	Other HC's in Decane Equiv. (ppm)
A	1	10/92		0.3	0.3	0.4	1.0	1.2
B	2	11/92					34.0	40.3
WI1	2	12/92					43.1	50.6
		05/93					51.3	55.5
WI2	2	12/92					53.6	63.3
BB1	1	11/92	0.3	0.1	0.1	0.2	0.8	1.0
BB2	1	10/92	0.3	0.4	1.0	0.7	2.2	2.6
		11/92	0.2	0.2	0.4	0.7	2.0	2.4
BB3	1	10/92	0.2	0.3	0.1	0.1	0.8	1.0
BB4	3	11/92					9.9	11.7
		12/92					8.3	9.7
BB5	1	11/92	0.2	0.3	0.4	0.4	1.2	1.5
BB6	1	11/92		0.1	0.3	0.4	0.4	0.5
		11/92		0.1	0.2	0.3	0.3	0.3

NMRI Bucket Code	Hydrocarbon Profile	Test Date (month/ year)	Butene (ppm)	Hexane (ppm)	Octane (ppm)	Decane (ppm)	Other HC's in Octane Equiv. (ppm)	Other HC's in Decane Equiv. (ppm)
BB7	1	11/92	0.3	0.2	0.2	0.3	0.8	0.9
		12/92	0.2	0.2	0.2	0.2	0.6	0.7
BB8	1	11/92	0.5	0.3	0.3	0.2	0.5	0.5
BB9	1	11/92	0.4	0.4	0.2	0.3	1.6	1.9
		12/92	0.2	0.2	0.1	0.2	1.3	1.5
BB10	1	11/92	0.3	0.2	0.5	0.6	1.4	1.7
G01	1	11/92		0.3	0.2	0.3	0.4	0.4
G02	1	11/92	0.2	0.5	0.2	0.2	0.5	0.6
		12/92	0.2	0.6	0.3	0.2	0.6	0.7
G03	1	11/92	0.2	0.2	0.4	0.5	1.1	1.4
G04	1	11/92	0.1	0.3	0.3	0.3	0.5	0.6
G05	1	11/92		0.2	0.2	0.4	0.7	0.9
G06	1	11/92		0.2	0.2	0.3	0.4	0.4
G07	1	11/92		1.3	0.3	0.4	0.9	1.1
G08	1	11/92		0.1	0.3	0.3	0.4	0.4
G09	1	11/92	0.1	0.5	0.3	0.1	0.4	0.4
		12/92	0.2	0.6	0.4	0.2	0.6	0.7

NMRI Bucket Code	Hydrocarbon Profile	Test Date (month/year)	Butene (ppm)	Hexane (ppm)	Octane (ppm)	Decane (ppm)	Other HC's in Octane Equiv. (ppm)	Other HC's in Decane Equiv. (ppm)
G10	1	11/92		0.1	0.1	0.2	0.4	0.4
		12/92		0.1	0.2	0.2	0.2	0.3
N5*	3	01/93	0.1	0.2	0.1		3.0	2.7
N6*	3	01/93	0.1	0.4	0.1		2.8	2.6
		05/93		0.1			5.0	5.5
GPE1**	3	01/93		0.2	0.1		1.7	1.5
GPE2**	3	01/93		0.3	0.2		3.3	3.1
Range			<0.1-0.5	<0.1-1.3	<0.1-1.0	<0.1-0.7	0.2-53.6	0.3-63.3
N			38	38	38	38	38	38
#Buckets	28							

1. *: non-indicating soda lime.
2. **: empty bucket.
3. Profiles detailed in text.
4. Values are reported to the nearest 0.1 ppm.
5. Blank concentrations are <0.1 ppm.
6. Accuracy of analysis is estimated to be +/- 30% relative.
7. Other HC's: other hydrocarbons, in addition to the 4 individual species, expressed both in terms of octane calibration response and decane response. Only one value should be used to consider contaminant levels in gas.

Table 2. Hydrocarbon contaminants measured with GC after 5 min of flow during washout experiments. Sodasorb® with and without indicator dye.

NMRI Bucket Code	Source	Hydrocarbon Profile	Test Date (month/year)	Decane (ppm)	Other HC's in Octane Equiv. (ppm)	Other HC's in Decane Equiv. (ppm)
B	FS	2	05/93		12.4	13.5
WI2	FS	2	03/93		13.4	12.6
BB4	FS-1, B-1	3	04/93		3.6	4.6
BB4C	FS-1, B-2	1	05/93			
BB4D	FS-1, B-1	3	04/93		7.1	7.8
BB4F	FS-1, B-2	1	05/93			
BB6	FS	1	05/93	0.1		
BB8	FS	1	04/93	0.1		
G08	FS	1	05/93	0.2		
N7	NI	3	05/93		2.7	3.1
N13	NI	3	04/93		2.9	3.3
Range				<0.1-0.2	<0.1-13.4	<0.1-13.5
N				11	11	11

1. Butene, hexane, and octane levels <0.1 ppm for all samples.
2. Profiles detailed in text.
3. Source: FS = Fleet supply,
FS-1 = same lot of Fleet supply,
B-1 = bucket manufactured same month,
B-2 = bucket manufactured different month than B-1.
NI = non-indicating soda lime.
4. Values are reported to the nearest 0.1 ppm.
5. Blank concentrations are <0.1 ppm.
6. Accuracy of analysis is estimated to be +/- 30% relative.
7. Other HC's: other hydrocarbons, in addition to decane, expressed both in terms of octane calibration response and decane response. Only one value should be used to consider contaminant levels in gas.

**Table 3. Hydrocarbon contaminants in bucket headspaces measured with GC.
Sofnoline® with indicator dye.**

NMRI Bucket Code/ Bucket Type	Hydrocarbon Profile	Test Date (month/ year)	Butene (ppm)	Hexane (ppm)	Octane (ppm)	Decane (ppm)	Other HC's in Octane Equiv. (ppm)	Other HC's in Decane Equiv. (ppm)
SL2/R	1	12/92		0.5	0.4	0.4	0.5	0.6
SL3/R	1	12/92		0.5	0.5	0.4	0.4	0.4
SL4/S	2	12/92	0.3				3.5	3.8
SL5/S	2	12/92					1.3	1.4
SL6/S	2	12/92	0.5				3.1	3.4
SL7/S	2	12/92					0.9	0.9
SL8/S	2	12/92					0.7	0.8
SL9/S	2	12/92					1.2	1.3
SL15/R	1	03/94		0.1	0.5	0.3	1.1	0.8
SL16/R	1	03/94		0.2	0.5	0.5	1.2	1.7
SL18/R	1	03/94	0.9	0.9	0.9	0.4	2.2	2.0
SL20/S	2	03/94					0.2	0.2
SL23/S	2	03/94					0.7	1.0
SL25/S	2	05/94					0.3	0.2
SL27/S	3	03/94			1.2		4.8	4.4
SL32/R	1	03/94	1.6	0.4	0.5	0.3	1.1	1.6

NMRI Bucket Code	Hydrocarbon Profile	Test Date (month/year)	Butene (ppm)	Hexane (ppm)	Octane (ppm)	Decane (ppm)	Other HC's in Octane Equiv. (ppm)	Other HC's in Decane Equiv. (ppm)
SL33/R	1	03/94	0.9	0.7	0.4	0.2	0.9	1.3
SL34/R	1	05/94	1.0	0.4	1.0	0.3	1.8	1.6
SL35/R	1	03/94	1.3	0.5	0.7	0.3	1.1	1.6
SL36/R	1	04/94	0.4	0.5	0.3	0.2	0.9	0.9
SL37/R	1	04/94	0.6	0.4	0.3	0.2	0.8	0.8
Range			<0.1-1.6	<0.1-0.9	<0.1-1.2	<0.1-0.5	0.2-4.8	0.2-4.4
#Buckets	21							

1. Profiles detailed in text.
 2. Values are reported to the nearest 0.1 ppm.
 3. Blank concentrations are <0.1 ppm.
 4. Accuracy of analysis is estimated to be +/- 30% relative.
 5. Other HC's: other hydrocarbons, in addition to the 4 individual species, expressed both in terms of octane calibration response and decane response. Only one value should be used to consider contaminant levels in gas.

Table 4. Soda lime contaminants measured with FTIR during washout experiments.

Sodasorb® with indicator dye.

NMRI Bucket Code	Source	Test Date (month/year)	Ammonia (ppm)	Ammonia washout (min)	Diethyl amine (ppm)	Ethyl amine (ppm)	Octane (ppm)	Octane washout (min)
B	FS	04/93	19.4	>71			12.4	45
		05/93	18.6	100			12.1	51
		12/93	17.1	82	3.0	<1	6.6	21
		02/94	12.7	72	3.0	<1	5.4	18
BB1	FS-1	05/93	28.4	>87			1.1	36
		11/93	25.3	>92	3.0	<1	0.5	
BB2	FS-1	04/93	19.2	71			1.1	24
		11/93	18.0	76	1.5	<1	0.9	
		11/93	17.7	62	1.6	<1	2.2	5
BB3	FS-2	06/94	13.0	43	0.8	<1	<0.5	
BB4	FS-2	04/93	13.3	>56			7.2	>56
BB4C	FS-2	05/93	20.0	51			0.8	
		12/93	22.1	52	1.3	<1	<0.5	
BB4D	FS-2	04/93	14.4	34			6.2	>54
		11/93	16.4	33	1.8	<1	5.0	52
		11/93	14.3	42	1.3	<1	4.4	72

NMRI Bucket Code	Source	Test Date (month/ year)	Ammonia (ppm)	Ammonia washout (min)	Diethyl amine (ppm)	Ethyl amine (ppm)	Octane (ppm)	Octane washout (min)
BB4F	FS-2	05/93	15.3	44			0.7	
BB5	FS-3	07/94	13.8	63	1.0	1.4	<0.5	
BB6	FS-3	04/93	8.8	>55			0.5	
		11/93	7.5	62	1.1	<1	0.5	
		12/93	5.4	62	0.6	<1	<0.5	
BB8	FS	04/93	16.4	>59			<0.5	
		05/93	16.8	61			0.9	
		09/93	18.7	77	1.7	<1	<0.5	
		11/93	16.4	72	1.7	<1	<0.5	
BB9	FS-4	05/93	26.1	71			1.1	36
BB10	FS-4	05/93	24.8	71			1.7	46
		12/93	20.4	82	1.9	<1	0.8	
C1	FS	05/94	24.3	112	3.7	1.4	0.7	
		07/94	26.8	93	4.3	1.4	0.8	
G01	FS	05/93	10.7	61			0.6	
		12/93	10.6	62	0.9	<1	0.5	
G02	FS	05/93	18.3	71			0.6	
		12/93	19.8	72	1.3	<1	<0.5	

NMRI Bucket Code	Source	Test Date (month/year)	Ammonia (ppm)	Ammonia washout (min)	Diethyl amine (ppm)	Ethyl amine (ppm)	Octane (ppm)	Octane washout (min)
G03	FS	06/93	29.0	>76			1.5	38
		09/93	23.6	82	2.1	<1	0.9	
		01/94	25.1	72	2.2	1.8	1.0	13
G04	FS	04/93	14.1	56			0.6	
		05/93	14.1	62			0.8	
		12/93	15.7	>62	1.0	1.1	0.6	
G06	FS	05/93	17.7	70			0.9	
		05/93	15.7	76			0.6	
		01/94	18.4	72	1.4	<1	0.5	
G07	FS	06/93	12.5	>66			0.7	
		01/94	14.8	62	1.6	2.0	0.5	
G08	FS	04/93	14.4	64			0.6	
		11/93	17.0	72	1.3	<1	0.7	
G09	FS	01/94	20.0	82	1.8	<1	<0.5	
G10	FS	06/93	13.4	>63			0.9	
		12/93	7.4	52	0.9	<1	<0.5	

NMRI Bucket Code	Source	Test Date (month/ year)	Ammonia (ppm)	Ammonia washout (min)	Diethyl amine (ppm)	Ethyl amine (ppm)	Octane (ppm)	Octane washout (min)
Mean (SD)			17.3 (5.4)		1.8 (0.9)			
Range			5.4-29.0	33-100	0.6-4.3	<1-2.0	<0.5-12.4	0-72
N			50	50	27	27	50	50
#Lots	16							
#Buckets	23							

1. Source: FS = Fleet supply,
FS-1 = same lot of Fleet supply,
FS-2 = same lot of Fleet supply,
FS-3 = same lot of Fleet supply,
FS-4 = same lot of Fleet supply.

1. Washout times = time to reach <1 ppm; > indicates washout not completed during experimental time.

2. Concentrations are maximum values during washout and are reported to the nearest 0.1 ppm.

3. Blank concentrations for amines indicate no measurement made.

4. Accuracy of analysis is estimated to be +/- 0.5 ppm for octane, ammonia, and diethyl amine, and +/- 1 ppm for ethyl amine.

Table 5. Intra-day precision for FTIR ammonia measurements of Sodasorb® with indicator dye.

NMRI Bucket Code	Test Date (month/year)	Maximum Ammonia Run 1 (ppm)	Maximum Ammonia Run (ppm)	Run1/Run2
B	12/93	17.1	16.8	1.02
BB1	11/93	25.3	26.0	0.97
BB2	11/93	18.0	17.6	1.02
BB4C	12/93	22.1	21.4	1.03
BB6	12/93	5.4	5.6	0.95
BB8	11/93	16.4	17.1	0.96
BB9	05/93	26.1	26.4	0.99
BB10	12/93	20.4	20.0	1.02
G01	05/93	10.7	10.7	1.00
"	12/93	10.6	10.9	0.98
G02	12/93	19.8	20.9	0.95
G03	01/94	25.1	24.6	1.02
G04	12/93	15.7	15.9	0.99
G06	01/94	18.4	18.9	0.97
G07	01/94	14.8	14.8	1.00
G08	11/93	17.0	16.9	1.01
G09	01/94	20.0	20.8	0.96
G10	12/93	7.4	7.4	1.01
Mean				0.99
Range				0.95-1.03
N				18

1. Runs 1 and 2 performed back-to-back on same day and completed in 3-6 h.

Table 6. Soda lime contaminants measured with FTIR during washout experiments. Sodasorb® without indicator dye.

NMRI Bucket Code	Test Date (month/year)	Ammonia (ppm)	Diethyl amine (ppm)	Ethyl amine (ppm)	Octane (ppm)	Octane washout (min)
N7	05/93	0.6			3.3	16
N8	04/93	0.7			2.8	11
	05/93	0.8			3.1	16
N13	04/93	0.7			2.2	16
	12/93	0.9	<0.5	<1	2.5	13
IP2	07/93	0.6			1.0	
	09/93	<0.5	<0.5	<1	1.0	
IP3	07/93	1.1			0.7	
IP4	08/93	0.6			1.6	14
IP5	08/93	<0.5			1.0	
IP6	08/93	<0.5	<0.5	<1	<0.5	
IP8	09/93	<0.5	<0.5	<1	0.6	
IPI0	08/93	<0.5			0.9	
	12/93	<0.5	<0.5	<1	0.7	
IP12	08/93	<0.5	<0.5	<1	<0.5	

NMRI Bucket Code	Test Date (month/ year)	Ammonia (ppm)	Diethyl amine (ppm)	Ethyl amine (ppm)	Octane (ppm)	Octane washout (min)
IP14	09/93	<0.5	<0.5	<1	1.2	17
Range		<0.5-1.1	<0.5	<1	<0.5-3.3	0-17
N		16	7	7	16	16
#Lots	8					
#Buckets	12					

1. Washout times = time to reach <1 ppm.
 2. Bucket code: IP2-IP14 contained soda lime in canister bags.
 3. Concentrations are maximum values during washout and are reported to the nearest 0.1 ppm.
 4. Blank concentrations for amines indicate no measurement made.
 5. Accuracy of analysis is estimated to be +/- 0.5 ppm for octane, ammonia, and diethyl amine, and +/- 1 ppm for ethyl amine.

Table 7. Soda lime contaminants measured with FTIR during washout experiments.
Sofnoline® with and without indicator dye.

NMRI Bucket Code	Test Date (month/year)	Ammonia (ppm)	Ammonia washout (min)	Diethyl amine (ppm)	Ethyl amine (ppm)	Octane (ppm)
SL3	10/93	0.7		<0.5	<1	0.6
SL3	10/93	0.7		<0.5	<1	0.5
SL3	02/94	0.7		<0.5	<1	0.6
SL12	02/94	1.7	52	1.1	1.1	0.7
SL13	02/94	1.1	18	0.9	1.0	0.7
SL14	02/94	2.0	42	<0.5	<1	0.5
SL15	02/94	1.1	17	<0.5	<1	0.8
SL16	02/94	1.0	19	<0.5	<1	0.7
SL17	02/94	0.8		<0.5	<1	0.7
SL18	02/94	0.5		0.9	1.2	0.6
SL19	02/94	1.3	42	<0.5	<1	<0.5
SL20	02/94	1.0		<0.5	<1	<0.5
SL21	02/94	2.7	72	3.4	1.0	<0.5
SL22	02/94	2.9	63	1.4	1.0	<0.5
SL23	02/94	0.5		<0.5	<1	<0.5

NMRI Bucket Code	Test Date (month/ year)	Ammonia (ppm)	Ammonia washout (min)	Diethyl amine (ppm)	Ethyl amine (ppm)	Octane (ppm)
SL24	02/94	0.6		<0.5	<1	<0.5
SL25	02/94	1.9	52	0.5	<1	<0.5
SL26	02/94	1.7	52	0.6	<1	<0.5
SL27	02/94	1.0		<0.5	<1	0.6
SL28	02/94	1.0	21	<0.5	<1	<0.5
SL29*	02/94	<0.5		<0.5	<1	<0.5
SL30	02/94	0.7		<0.5	<1	<0.5
SL31*	03/94	<0.5		<0.5	<1	<0.5
SL32	03/94	2.0	53	0.6	<1	0.6
SL33	03/94	2.2	52	0.6	1.4	<0.5
SL34	03/94	2.5	63	2.1	1.3	0.6
SL35	03/94	2.2	52	0.6	1.3	0.6
Range	10/93- 03/94	>0.5-2.9	0-72	<0.5-3.4	<1-1.4	<0.5-0.8
N		27	15	27	27	27
#Lots	19					
#Buckets	25					

1. Washout times = time to reach <1 ppm.
2. Concentrations are maximum values during washout and are reported to the nearest 0.1 ppm.
3. Accuracy of analysis is estimated to be ± 0.5 ppm for octane, ammonia, and diethyl amine, and ± 1 ppm for ethyl amine.
4. *: reduced dye

**Table 8. Ethyl violet dye
concentrations of Sodasorb® with
indicating dye.**

NMRI Bucket Code	Test Date (month/year)	Ethyl violet (%)
BB1	05/94	0.018
BB3	05/94	0.015
BB4D	05/94	0.011
BB5	05/94	0.016
C1	05/94	0.030
G01	05/94	0.018
G02	05/94	0.021
G09	05/94	0.027
G10	05/94	0.018
Mean (SD)		0.019 (0.006)
Range		0.011-0.030
N		9
#Lots		9

**Table 9. Ethyl violet dye
concentrations of Sofnolime® with
indicating dye.**

NMRI Bucket Code	Test Date (month/year)	Ethyl violet (%)
SL3	03/94	0.018
SL10	04/94	0.017
SL11	04/94	0.020
SL12	04/94	0.022
SL13	04/94	0.019
SL14	04/94	0.022
SL16	03/94	0.018
SL17	04/94	0.016
SL20	04/94	0.023
SL22	04/94	0.022
SL23	04/94	0.019
SL26	04/94	0.022
SL27	04/94	0.021
SL28	04/94	0.023
SL30	04/94	0.024
SL32	04/94	0.023
SL33	04/94	0.022
SL34	04/94	0.026
SL35	03/94	0.022
SL36	04/94	0.022
SL37	04/94	0.023
SL38	04/94	0.023
SL39	04/94	0.022

NMRI Bucket Code	Test Date (month/year)	Ethyl violet (%)
Mean (SD)		0.021 (0.002)
Range	3/94-4/94	0.016-0.026
N		23
#Lots		23

Appendix A. Sodasorb® buckets tested.				
NMRI Bucket Code	Manufacturer Lot Number	Lot Date (month/ year)	Bucket Date (month/ year)	Lid Date (month/ year)
A	AA04-4004-12	04/91	01/91	03/91
B	AA08-4004-29	08/91	07/91	08/91
WI1	"	08/91	07/91	07/91
WI2	"	08/91	07/91	07/91
BB1	AB02-4004-28A	02/92	01/92	01/92
BB2	"	02/92	12/91	01/92
BB3	AB02-4004-06	02/92	12/91	11/91
BB4	"	02/92	10/91	11/91
BB4C	"	02/92	12/91	11/91
BB4D	"	02/92	10/91	11/91
BB4F	"	02/92	12/91	11/91
BB5	AB05-4004-18	05/92	12/91	03/92
BB6	"	05/92	03/92	03/92
BB7	AB05-4004-28	05/92	12/91	03/92
BB8	"	05/92	12/91	03/92
BB9	AB02-4004-28	02/92	12/91	01/92
BB10	"	02/92	12/91	01/92
C1	AB04-4004-28A	04/92	12/91	
G01	AB07-4004-6A	07/92	03/92	03/92
G02	AB07-4004-9	07/92	07/92	03/92
G03	AB06-4004-5	06/92	12/91	03/92
G04	AB07-4004-7	07/92	03/92	03/92
G05	"	07/92	03/92	03/92
G06	AB06-4004-2	06/92	12/91	04/92
G07	AB06-4004-9	06/92	03/92	04/92
G08	AB07-4004-6	07/92	07/92	03/92

NMRI Bucket Code	Manufacturer Lot Number	Lot Date (month/ year)	Bucket Date (month/ year)	Lid Date (month/ year)
G09	AB07-4004-8A	07/92	07/92	07/92
G10	AB07-4004-8	07/92	03/92	03/92
N5*	AB11-B600-19	11/92	11/92	11/92
N6*	"	11/92	11/92	11/92
N7*	"	11/92	09/92	12/92
N8*	"	11/92	09/92	12/92
N13*	"	11/92	09/92	12/92
IP2*,cb	AC06-4036-30	06/93	06/93	
IP3*,cb	AC07-4036-1	07/93	06/93	
IP4*,cb	AC06-4036-30	06/93	06/93	06/93
IP5*,cb	AC07-4036-2	07/93	06/93	06/93
IP6*,cb	AC07-4036-28	07/93	07/93	07/93
IP8*,cb	AC07-4036-12	07/93	07/93	06/93
IP10*,cb	AC07-4036-9	07/93	07/93	
IP12*,cb	AC07-4036-15	07/93	07/93	07/93
IP14*,cb	AC07-4036-2	07/93	06/93	06/93
GPE1**			09/92	11/92
GPE2**			09/92	11/92
Range		04/91- 07/93	01/91- 07/93	03/91- 07/93
#Lots	25			
#Buckets	44			
1. *: non-indicating soda lime. 2. **: empty bucket. 3. cb: packaged in canister bags which were then put inside the bucket.				

**Appendix B. Sofnolime® buckets
tested.**

NMRI Bucket Code/ Bucket Type	Manufacturer Lot Number	Lot Date (month/ year)	Bucket Date (month/ year)
SL1/S	165092	09/92	06/92
SL2/R	005102G	10/92	
SL3/R	"	10/92	10/92
SL4/S	260091	09/91	
SL5/S	165092	09/92	
SL6/S	479111	11/91	
SL7/S	956072	07/92	
SL8/S	166092	09/92	
SL9/S	"	09/92	
SL10/R	004102G	10/92	10/92
SL11/R	006102G	10/92	10/92
SL12/R	007102G	10/92	10/92
SL13/R	018112G	11/92	10/92
SL14/R	198063G	06/93	05/93
SL15/R	016112G	11/92	10/92
SL16/R	"	11/92	10/92
SL17/R	134043G	04/93	12/93
SL18/R	"	04/93	12/93
SL19/S	166092	09/92	06/92
SL20/S	"	09/92	06/92
SL21/S	165092	09/92	06/92
SL22/S	"	09/92	06/92
SL23/S**	607033	03/93	12/92
SL24/S**	"	03/93	12/92
SL25/S**	348112	11/92	03/92

NMRI Bucket Code/ Bucket Type	Manufacturer Lot Number	Lot Date (month/ year)	Bucket Date (month/ year)
SL26/S**	348112	11/92	03/92
SL27/S	120082	08/92	03/92
SL28/S	119082	08/92	03/92
SL29*/S	522013	01/93	06/92
SL30/S	118082	08/92	06/92
SL31*/S**	323123	12/93	12/92
SL32/R	166053G	05/93	11/92
SL33/R	170053G	05/93	04/93
SL34/R	163053G	05/93	11/92
SL35/R	162053G	05/93	11/92
SL36/R	172053G	05/93	04/93
SL37/R	169053G	05/93	04/93
SL38/R	038122G	12/92	11/92
SL39/R	145043G	04/93	01/93
Range		09/91- 12/93	03/92- 12/93
#Lots	28		
#Buckets	39		
1. Bucket type: S = square, R = round. 2. *: non-indicating soda lime. 3. **: 8-12 mesh granules; all other buckets 4-8 mesh.			

FIGURE LEGENDS

Figure 1. Diagram of test apparatus for measuring contaminant washout as humidified gas flowed through a bed of soda lime. The standard open-circuit test flushed contaminants from the system. The special closed-circuit test recirculated the gas flowing out of the soda lime back into the bed using a stainless steel bellows pump; this application is not discussed in this report.

Figure 2. Volatile hydrocarbon contaminants found in the headspace of Sodasorb® buckets. Representative ion chromatograms (GC/MS data; 35 to 200 amu) of the 3 different hydrocarbon profiles found in buckets containing Sodasorb® and profile 3 found in a "virgin" bucket that never was exposed to soda lime.

FIGURE 1

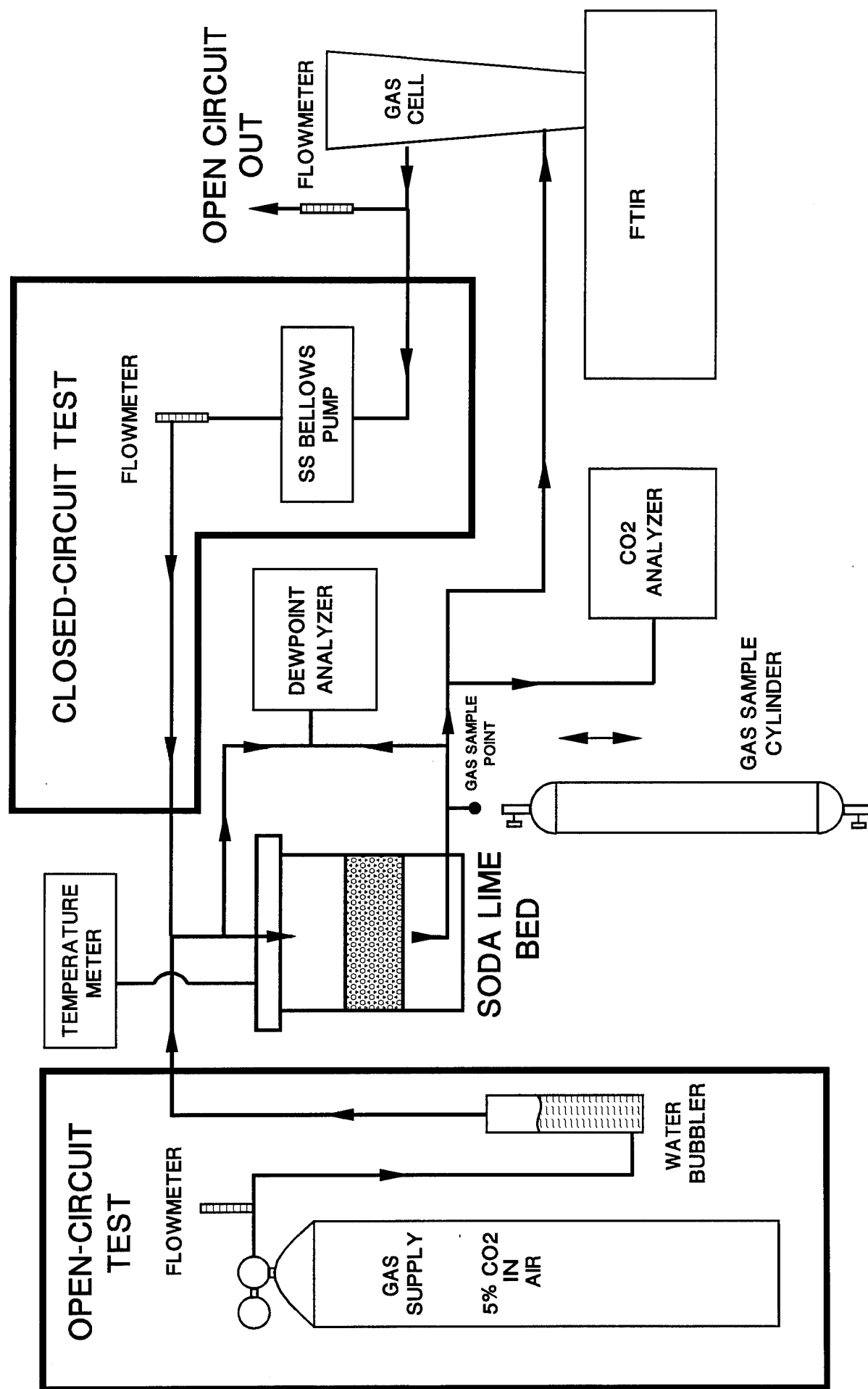


FIGURE 2

